

EXPLOSIVES AND PYROTECHNIC PROPELLANTS FOR USE IN  
LONG TERM DEEP SPACE MISSIONS\*

Carl S. Gorzynski, Jr. (i)

and

J. Norman Maycock (ii)

Martin Marietta Corporation  
Martin Marietta Laboratories  
1450 South Rolling Road  
Baltimore, Maryland 21227

N74-13664

Unclas  
24094

63/33

(NASA-CR-132373) EXPLOSIVES AND  
PYROTECHNIC PROPELLANTS FOR USE IN LONG  
TERM DEEP SPACE MISSIONS (Martin Marietta  
Corp.) 31 p HC \$3.75 CSCL 19A

\* Supported by NASA, Langley Research Center, Contract No. NAS1-10698.  
Spacecraft Sterilization, Properties of Materials.

(i) Senior Associate Research Scientist, Chemistry Department.

(ii) Associate Director and Head of Chemistry Department.

Associate Fellow AIAA. Member AIAA TC, Propellants and Combustion.

## ABSTRACT

Explosives and pyrotechnic propellant materials which will withstand heat sterilization cycling at 125°C and ten year deep space aging under  $10^{-6}$  torr and 66°C have been selected. The selection was accomplished through a detailed literature survey and an analytical evaluation of the physicochemical properties of the materials. The chemical components of the electroexplosive devices used in U.S. missiles and spacecraft were categorized into primary explosives, secondary explosives, and propellant ingredients. Kinetic data on such parameters as thermal decomposition and sublimation were obtained for these materials and used as a basis for the ten year life prediction. From these experimental data and some analytical calculations, a listing of candidate materials for deep space missions was made.

## INTRODUCTION

Future long-term deep space missions, such as the exploration of the outer planets, necessitate the spacecraft being exposed to deep space environments for periods of up to ten years. The explosive and propellant actuated devices on board used to perform mechanical functions must survive these exposures and exhibit a predictable performance. More specifically, the chemical components (i. e. the explosive and pyrotechnic propellant materials) in the devices must maintain their initial characteristics throughout the mission.

Under relatively high sterilization temperatures (e. g. two 64 hour cycles at 125°C) and on prolonged exposure to an outer space environment (e. g. 10 years at 66°C\* under 10<sup>-6</sup> torr) these chemical components could experience several physical changes. It is conceivable that materials having relatively high vapor pressures will sublime away from initiating interfaces, thus creating voids and potential functional failures. For example, the exposed material at the open ends of mild detonating fuse leads, (MDF), may evaporate and be deposited onto some foreign surface. Also, after storage at an elevated temperature for periods of up to 10 years, the degree of thermal decomposition of the materials may be significant enough to affect the performance of the device. Additionally, since many ordnance devices contain several explosives, any material that would melt during sterilization or during the flight could, upon cooling, cause various eutectic mixtures to be formed, and resultant performance changes.

---

\*Caused by solar radiation or onboard radioisotope thermoelectric generated<sup>or's</sup> (RTGs).

To determine the survivability of materials to be used in long term deep space missions each item must be tested. Since heat sterilization is accomplished in a few days, laboratory tests duplicating the sterilization requirements may easily be performed.<sup>1-6</sup> However, since real-time aging and either performance testing of the devices or analytical (chemical) testing of the components to determine their survivability and reliability after several years' aging is not practicable, an accelerated aging technique must be used.

Studies have been and are being performed wherein explosives and propellants undergo "accelerated aging".<sup>7-11</sup> These studies are directed at determining the effects of age on the performance of devices or propellants and at establishing the maximum safe storage life. However, in these studies, "accelerated aging" is the storage of an explosive or propellant actuated device at some arbitrarily chosen temperature above ambient, typically 50 to 80°C, under ambient pressure, for periods ranging from 1 to 3 years. The philosophy of this approach is that if the items survive storage at an elevated temperature for a particular length of time then they will survive for longer periods of time at a lower storage temperature.

The most quantitative accelerated aging method that has been proposed thus far<sup>12</sup> is based on a modification of the Arrhenius reaction rate equation. This method assumes that if a material survives a certain length of time at some elevated temperature, then this survival time increases by a factor of between 2.7 and 2.9 for every 10°C decrease in temperature. In this technique it is further assumed that the reaction rate for all materials increases by a factor of between 2 and 3

for each  $10^{\circ}\text{C}$  rise in temperature.

In none of these accelerated aging studies is any reference made to the possibility that a change may occur in the activation energy of the critical degradation process with temperature.

An accelerated aging procedure can only be meaningful when the critical degradation process occurring at the elevated test temperature is truly the same process which occurs at the actual storage temperature. The relationship between the rate of a degradation process and temperature may not be a single linear relationship, but instead be two or even more linear relationships. One example of this can be seen with PETN, where the plot of  $\log$  (% weight loss) against reciprocal temperature gives two straight lines with the break occurring at the melting point<sup>13</sup>. In such a case, any accelerated aging above the melting point would be meaningless because the accelerated test would be monitoring a reaction completely different from the one occurring in real aging. Another example of this can be seen in the thermal decomposition of ammonium perchlorate (AP). Below approximately  $300^{\circ}\text{C}$  AP undergoes decomposition such that only 30% of the starting material is decomposed, whereas above  $300^{\circ}\text{C}$  the reaction goes to completion with a different activation energy. It is, therefore, extremely important that the temperature chosen for the accelerated aging tests be within the temperature range applicable to the chemical reaction occurring in real-time aging.

Basically, the processes involved in aging can be described in terms of solid state kinetics, so it is possible to deduce a meaningful and correct aging from data on the parameters relating to the physicochemical properties of the materials such as thermal decomposition kinetics, sublimation kinetics, phase change characteristics, change of state phenomena, etc. These decomposition and sublimation kinetics, when available, can be used to predict material losses up to a ten year period under deep space environment exposures. When these kinetic data are not available, an analytical approach to determine these parameters can be used. Since explosive and propellant materials stored for years in a vacuum at some elevated temperature will experience degradation through sublimation and/or thermal decomposition, two parameters of major interest are the rates of these two processes.

The rate at which a material decomposes thermally is determined by the rate constant,  $k$ , whose thermal dependence is given by

$$k = A \exp^{-E/RT} \quad (1)$$

where  $k$ , the reaction rate constant is expressed in units of  $\text{sec}^{-1}$ ,  $E$  is the activation energy in  $\text{kcal mole}^{-1}$ ,  $T$  the absolute temperature, and  $A$  an experimentally determined frequency factor. If the fractional decomposition,  $\alpha$ , under isothermal conditions, can be determined as a function of time,  $t$ , then  $k$  can be evaluated. Several equations have been derived to describe the complete  $\alpha - t$  curves<sup>14</sup> such that accurate

linear plots can be obtained up to  $\alpha = 0.99$ . For our purposes we are only interested in  $\alpha$  values of 0.10 which enables us to use the simple expression

$$t = \ln (1 - \alpha) / k \quad (2)$$

for all cases. This is still an approximation of correctness but any error due to invalidity of the equation will be small.

The degree of sublimation exhibited by a material can be determined by the Langmuir method,<sup>15</sup> using the expression

$$G = \frac{P}{17.14} \sqrt{\frac{M}{T}} \quad (3)$$

where G is the rate of sublimation in gm. cm. <sup>-2</sup> sec. <sup>-1</sup>, P is the vapor pressure in Torr, M the molecular weight, and T the absolute temperature. The vapor pressure of a material, if it cannot be extracted from experimental data, can be derived from the vapor pressure equation<sup>16</sup> expressed as

$$\log P = A + B/4.576T \quad (4)$$

where A and B are experimentally determined constants, A being a frequency factor and B the activation energy associated with the process, and T is the absolute temperature.

By using data available in the literature and these analytical expressions on explosive and pyrotechnic propellant materials, a selection of candidate materials most likely to survive sterilization

and long term deep space aging can be made. In this study the explosive components of the electroexplosive devices used in NASA, Army, Navy, and Air Force systems were identified, and categorized into primary explosives, secondary explosives and propellant ingredients, and then, along with some available but as yet unused explosives, evaluated for qualification as candidates. The qualification of a material as a candidate for long term deep space missions has been based upon its ability to survive (1) two 64 hour sterilization heat cycles at 125°C and (2) storage for ten years at 66°C under a pressure less than  $10^{-6}$  Torr.

## RESULTS AND DISCUSSION

### a. Primary Explosives

Ten primary explosives were surveyed (Table 1). For six of these - lead styphnate, barium styphnate, LDNR, LMNR, TPB, and KDNEBF\* - insufficient data are available to determine whether or not they would withstand the specified heat sterilization and deep space storage conditions.

Lead styphnate loses its water of hydration readily at elevated temperatures<sup>17,18</sup>, although after heat sterilization of three 36-hour cycles at 145°C 24 devices with lead styphnate, ignition elements fired without failure<sup>3</sup>. Whether it will lose its water of hydration upon deep space storage to an extent that would lead to non-uniformity and erratic behavior is questionable. Since in general the properties and the stability of barium styphnate<sup>19</sup> are very

---

\*Acronyms are defined in Tables 1 and 2.

similar to lead styphnate, the same reservation applies to it.

LDNR and LMNR are anhydrous and less volatile than the styphnates<sup>20</sup>, so may survive sterilization, however, their long term deep space stability is indeterminable from the limited short term thermal and vacuum stability data available<sup>3, 21</sup>.

The only data available on TPB are that it melts at 386°C, remains stable after 2 hours at 300°C, and exhibits several phase transitions<sup>22</sup>. More explicit data on the properties of its different phases, especially volatility, must be obtained.

Only short term vacuum stability<sup>23</sup> and thermal stability (at 100°C)<sup>24</sup> tests have been performed on KDNBF.

These six explosives are therefore labeled as questionable candidates until more data relevant to the specified environments are available to make a firm decision. For the remaining four primaries- DDNP, black powder, lead azide, and copper azide- sufficient data are available to indicate that they would not survive the specified environments.

DDNP, for instance, in vacuum at 120°C is completely decomposed in less than 24 hours, and at 110°C decomposition is complete in 80 hours<sup>25</sup>. These temperatures and times are well below those specified for sterilization. The melting point of the sulfur in the black powder is also below the sterilization temperature. Additionally, because of the high volatility of sulfur it is possible that under the specified deep space storage constraints it will sublime from the black powder leaving an inhomogeneous mixture.

Even though lead azide is perhaps the most widely used primary explosive in military applications, its instability<sup>26,27</sup> and compatibility<sup>28</sup> limit its immediate qualification as a candidate. Numerous cases of spontaneous explosion of lead azide are known, e. g. during pouring, weighing, drying, and even upon storage<sup>24</sup>. The extreme sensitivity and instability are counteracted in the commercial product by the addition of small amounts of lead hydroxide and dextrin. This form, known as "dextrinated lead azide", has the approximate composition: lead azide, 93%; lead hydroxide, 4%; dextrin and impurities, 3%. Dextrinated lead azide, however, is less thermally stable than pure lead azide. At 75°C it loses approximately 0.8% of its weight during the first four days, after which further heating involves a loss of 0.03 - 0.05% per week<sup>30</sup>. Should this degradation continue at this rate, in 10 years this amounts to a 15 to 25% loss. At the specified storage temperature (66°C) the amount of material lost for the same time period will be only slightly less. For missions relevant to this study it is probable that lead azide of a pure form, e. g. polyvinyl alcohol lead azide or RD1333 lead azide could be used. Lead azide is unique and in many cases necessary in an explosive train design to achieve detonation in short columns. Thus lead azide, of a pure form, could qualify for long term space missions.

Although copper azide is not widely used, its high shock sensitivity eliminates it as a candidate. Copper azide is exceptionally sensitive to friction and is often exploded by contact. It is also very sensitive to impact, and is exploded by a 2 kg weight falling from a height of less than 1 cm<sup>31</sup>. Associated with this high sensitivity, copper azide is known to be extremely unpredictable in its explosive stability<sup>32</sup>.

Again, although sufficient data are available to disqualify four of the ten primary explosives surveyed, the remaining six cannot positively be either qualified or disqualified until more data are made available, particularly on their long term thermal stability.

#### b. Secondary Explosives

The secondary explosives surveyed are listed in Table 2. As indicated in the Table, only eight different secondary explosives are being utilized in aerospace and military electroexplosive devices - DIPAM, HMX, HNS, nitrocellulose, nitroglycerine, PETN, RDX, and TACOT. In the process of surveying and evaluating these eight explosives along with several available but as yet unused explosives, some limited information and data were examined for six explosives not yet available commercially. These six are newly developed high temperature resistant explosives, and the data on them are mostly in the form of synthesis procedures and crystallographic structure determinations. However, the limited amount of stability data that are available at this time indicate that these materials are potential candidates, and that further studies on them may conclusively demonstrate their qualification.

Vapor pressure and sublimation data are reported in the literature for only nine secondary explosive materials. Of these nine, five are currently used in devices - HNS, DIPAM, HMX, RDX, and PETN. The remaining four - TATB, DATB, TNA, and TNT - are available but as yet unused. Table 3 lists the vapor pressure,

sublimation rate, and anticipated ten year weight loss determined for these materials at the specified storage temperature, 66°C. Data on ammonium perchlorate (AP) are included in the Table for comparison because of its extensive use as a propellant ingredient in many initiators and igniters. The table shows that among the currently used explosives there is an extremely wide range of material losses, and the relatively large losses of RDX and PETN are serious enough to disqualify these materials.

A comparison of the change in vapor pressure as a function of temperature for the materials listed in Table 3 is given in Figure 1. The curves were generated from the reported vapor pressure equations of each material. Again, among the currently used explosives large differences extending over several orders of magnitude can be seen. A further comparison of the five used explosives, in the amount of weight lost through sublimation as a function of temperature, is given in Figure 2, where equation(3) was used to generate the data. The relatively high volatility of RDX and PETN which disqualifies them as candidates can be seen. After ten years at the specified storage temperature of 66°C, RDX and PETN, will sublime approximately 20 gm/cm<sup>2</sup> and 890 gm/cm<sup>2</sup>, respectively, while HNS, HMX, and DIPAM by comparison will sublime approximately  $6 \times 10^{-7}$ ,  $10 \times 10^{-7}$ , and  $2.6 \times 10^4$  gm/cm<sup>2</sup>.

Further reasons for the disqualification of RDX and PETN can be seen in Figures 3 and 4 where the time in which HMX, RDX, and PETN will thermally decompose 1% and 10% as a function

of temperature is presented. Since the activation energies and Arrhenius constants used in equation (1) to generate the curves in these figures were experimentally determined at temperatures generally between 200 and 300°C, the rate constants for the required lower temperatures must be considered as approximate. At the specified sterilization temperature, 125°C, these data indicate PETN will decompose 10% in about 18 hours and RDX will decompose 10% in about 0.1 years. At the specified storage temperature however, RDX will decompose only 1% in about 300 years, and PETN 1% in about 10 years. In comparison, the amount of HMX decomposition at these temperatures is negligible.

Four additional secondary explosives which do not qualify as candidates are TNA, TNT, nitroglycerine, and nitrocellulose. As seen in Table 3 and Figure 1, TNA is more volatile and less thermally stable than RDX, and TNT more volatile and less stable than PETN. Since RDX and PETN were disqualified as discussed above, so TNA and TNT are also disqualified as candidates. Nitroglycerine is disqualified because it is an extremely volatile liquid, unsuitable for spacecraft use. Nitrocellulose has a relatively low thermal stability, is more volatile than PETN, and at 134.5°C explodes in 300 minutes<sup>38</sup>, so is therefore disqualified. Thus, of the eight secondary explosives that are being utilized in devices only four qualify as candidates - HNS, DIPAM, HMX, and TACOT. Also, of the four available but as yet unused secondary explosives for which sublimation and thermal decomposition data are available

only two qualify - TATB and DATE.

For the remaining available but unused secondary explosives specific sublimation and thermal decomposition data are not available, but the chemical and thermal stability data available indicate that two of these secondaries - nonanitroterphenyl and octanitroterphenyl - will withstand the specified heat sterilization and deep space storage constraints. For the other explosives in this group the limited amount of stability data indicate that these materials are potential candidates and that further studies may clearly show them to be qualified.

#### c. Pyrotechnic Propellant Materials

Presently, eighteen different inorganic materials, six metals, one metal alloy, and three organic materials are being used as pyrotechnic propellant ingredients in ordnance devices (Table 4).

Although sublimation and vapor pressure data are available on only three of the eighteen inorganic materials (ammonium perchlorate<sup>35</sup>, molybdenum trioxide<sup>39</sup>, and silicon dioxide<sup>40</sup>) and only limited thermal decomposition data have been reported for these materials, they are in general quite stable at the specified sterilization and storage temperatures. Only two materials remain questionable--ammonium dichromate and lead thiocyanate. The only applicable data available on ammonium dichromate and lead thiocyanate are that they decompose at 170°C and 190°C respectively.<sup>41</sup> All of the other inorganics being used melt or begin decomposing at 300°C

and higher. Since ammonium dichromate and lead thiocyanate have relatively low decomposition temperatures, their decomposition rate constant may be high enough such that after ten years at the specified storage temperature, they would be significantly or perhaps even completely decomposed. Thus, the data on ammonium dichromate and lead thiocyanate at this time are insufficient to either qualify or disqualify them as candidates.

The six metals and one metal alloy currently in use are aluminum, boron, magnesium, titanium, tungsten, zirconium, and zirconium/nickel. Aluminum and magnesium melt at 659°C and 651°C, respectively, while the remaining five melt between 1500 and 3400°C<sup>42</sup>. The temperatures at which the metals have a vapor pressure of 10<sup>-11</sup> torr<sup>42</sup> are: aluminum-542°C, boron-1062°C, magnesium-115°C, Nickel-767°C, titanium-807°C, tungsten-1777°C, and zirconium-1227°C. None of the metals will melt, sublime, or decompose under the specified sterilization and deep space storage conditions. With the data that are available so far, there are no indications of any compatibility problems with these metals in propellant ingredients. These six metals and one metal alloy therefore qualify as candidates.

Teflon, Viton A, and Viton B are the three organic materials presently being used as pyrotechnic propellant materials along with metals and metal oxides in initiator and igniter compositions. Teflon is extremely inert and stable up to temperatures of 250°C.<sup>43, 44</sup> At temperatures above 250°C it begins to decompose very slowly. The initial rate of weight loss is 0.0001% per hour at

260°C, and 0.004% per hour at 370°C.<sup>45</sup> Viton A and Viton B also display outstanding resistance to degradation by heat, with Viton B possessing better high temperature resistance than Viton A.<sup>46,47</sup> After 3 days at 200°C in air, Viton A had a 1.4% weight loss, but, for the same time and temperature in vacuum it had a 0.45% weight loss.<sup>48</sup> After 24 hours at 260°C, raw Viton had a 1% weight loss in air and a 0.7% weight loss in nitrogen.<sup>48</sup> In view of the way these three organic materials -- Teflon, Viton A, and Viton B -- are being used, along with their temperature stability, they qualify as candidates.

### CONCLUSIONS

Many explosive and pyrotechnic propellant materials are available which appear to be capable of surviving heat sterilization and ten year deep space flight times without deterioration. When data on the parameters relating to the physicochemical properties of these materials such as thermal decomposition kinetics, sublimation kinetics, change of state phenomena, etc. are available the chemical and thermal stability of these materials under the specified environments can be determined. Unfortunately, these types of data are available for only a small number of explosive materials and therefore just a few secondary explosives and propellant ingredients can be definitely qualified as candidate materials (Table 5) capable of withstanding the specified environments. The limited amount of relevant data that are available on a larger number of primary and secondary explosives is sufficient to qualify these materials conditionally. Further data and/or testing are required for definite qualification.

## REFERENCES

1. Montgomery, L. C., "Sterilization of Solid Propellants," Rept. SPS 37-20, Vol. IV, April 30, 1963, pp. 58-60, Jet Propulsion Lab., Pasadena, Calif.
2. Benedict, A. G., "Development of Sterilizable Pyrotechnic Devices," Rept. SPS 37-32, Vol. IV, April 30, 1965, pp. 112-114, Jet Propulsion Lab., Pasadena, Calif.
3. Bowman, N. J. and Knippenberg, E. F., "The Sterilization of Pyrotechnic Devices," Rept. 65SD992, December 23, 1965, General Electric Co., Missile and Space Div., Philadelphia, Pa.
4. Bowman, N. J. and Knippenberg, E. F., "Pyrotechnic Devices for Use on Sterilized Spacecraft," Journal of Spacecraft and Rockets, Vol. 3, No. 10, Oct. 1960, pp. 1542-1544.
5. Lukens, S. C., "Sterilizable Liquid Propulsion System," Journal of Spacecraft and Rockets, Vol. 6, No. 6, June 1969, pp. 717-722.
6. Bement, L. J., "Sterilization-Environmental Testing of Initiators," Proceedings of the Sixth Symposium on Electroexplosive Devices, San Francisco, Calif., July 1969, pp. 3-3.1 -3-3.15.
7. Donnard, R. E., "Standardization of Lead Styphnate Primers, Priming Mixtures and Processes," Report R-1494, June 1959, Frankford Arsenal, Research and Development Group, Philadelphia, Pa.
8. Roth, M. and Younginger, M. R., "Prediction of the Effects of Storage on ARP Propellant By means of Chemical Analysis," Technical Note FRL-TN-126, March 1962, Picatinny Arsenal, Feltman Research Lab., Dover, N. J.
9. Biddix, B. D., "Igniter Mark 280 Mod 0 for Use in Rocket Motor Mark 32 Mod 0 (HASP): Qualification Test Report," Technical Report 272, August 20, 1968, U. S. Naval Ordnance Station, Indian Head, Md.
10. Koster, D. R., "Igniter Mark 192 Mod 2 Type-Life Program: Final Report," Technical Report 299, August 15, 1969, U. S. Naval Ordnance Station, Indian Head, Md.
11. MacDonald, R., "The Effect of Environment on the Accelerated Aging of Gun Propellants," Report R-612/70, February 1970, Defense Research Establishment Valcartier, Quebec, Canada.
12. Moses, S. A., "Accelerated Life Test for Aerospace Explosive Components," Proceedings of the Seventh Symposium on Explosives and Pyrotechnics, Philadelphia, Pa., September 1971, pp. II-3-1 - II-3-8.

13. Maycock, J.N. and Pai Verneker, V.R., "Characterization of Thermal and Photosublimation of Organic Explosives by Thermobarogravimetric Techniques," *Thermochimica Acta*, Vol. 1, No.2, May 1970, pp. 191-198.
14. Palanisamy, T. et al., "Kinetics of Thermal Decomposition of Some Metal Oxalates," *Thermochimica Acta*, Vol.2, No. 3, May 1971, pp. 265-273.
15. Langmuir, I., "The Vapor Pressure of Metallic Tungsten," *The Physical Review, Second Series*, Vol.II, No.5, Nov. 1913, pp.329-342.
16. Dushman, S., "Scientific Foundations of Vacuum Technique," Wiley, New York, 1955, pp.18-24, 740-743.
17. Hailes, H. R., "The Thermal Decomposition of Lead Styphnate," *Transactions of the Faraday Society*, Vol.29, Part 4, April 1933, pp.544-549.
18. Tompkins, F. C. and Young, D.A., "The Decomposition of Lead Styphnate Monohydrate," *Journal of the Chemical Society*, Publication No.647, 1956, pp. 3331-3332.
19. Tompkins, F. C. and Young, D.A., "The Decomposition of Barium Styphnate Monohydrate," *Transactions of the Faraday Society*, Vol. 52, Part 7, July 1956, pp.1245-1254.
20. Rinkenback, W.H., "Explosives," *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Vol. 8, Wiley, New York, 1968, p.591.
21. "Engineering Design Handbook, Explosive Series, Properties of Explosives of Military Interest," Pamphlet AMCP 706-177, March 1967, pp.190-192, U.S. Army Materiel Command, Washington, D. C.
22. Hudson, F.M., Chemtronics, Inc., Asheville, North Carolina, Private Communication.
23. Costain, T.S., "Investigation of Potassium Dinitrobenzofuroxan (KDNBF) to Provide Data Necessary for the Preparation of A Military Specification," Technical Report 4067, November 1970, Picatinny Arsenal, Dover, N.J.
24. Reference 21, pp.182 - 186 .
25. Vaughn, J. and Phillips, L., "Thermal Decomposition of Explosives in the Solid Phase. Part I.," *Journal of the Chemical Society*, Publication No. 306, 1947, pp. 1560-1565.
26. Avrami, L. and Jackson, H. J., "Results of Laboratory Studies on Triex-8 Dextrinated Lead Azide," Technical Memorandum 1877, February 1969, Picatinny Arsenal, Dover, N.J.
27. Pai Verneker, V.R. and Maycock, J.N., "Simultaneous Differential Thermal Analysis-Thermogravimetric Analysis Technique to Characterize the Explosivity of Lead Azide," *Analytical Chemistry*, Vol. 40, No. 8, July 1968, pp. 1325-1329.

28. Rosen, J. and Simmons, H. T., "Compatibility of Inorganic Azides with Organic Explosives," I & EC Product Research and Development, Vol. 7, No. 4, December 1968, pp. 262-264.
29. Urbanski, T., "Chemistry and Technology of Explosives," Vol. 3, Pergamon Press, New York 1967, pp. 173-176.
30. Ibid., p. 172.
31. Ibid., p. 185.
32. Yoffe, A. D., "Thermal Decomposition and Explosion of Azides," Proceedings of the Royal Society of London, Series A, Vol. 208, No. A 1093, January 1951, pp. 188-199.
33. Rosen, J. M. and Dickinson, C., "Vapor Pressures and Heats of Sublimation of Some High Melting Organic Explosives," Journal of Chemical and Engineering Data, Vol. 14, No. 1, January 1969, pp. 120-124.
34. Kamlet, M. J., "Perspectives and Prospects for Research in High Energy Chemistry in 1966-1975. I. Heat Resistant Explosives, Technical Report 65-220, May 24, 1966, U. S. Naval Ordnance Laboratory, White Oak, Md.
35. Guirao, C. and Williams, F. A., "Sublimation of Ammonium Perchlorate," Journal of Physical Chemistry, Vol. 73, No. 12, December 1969, pp. 4302-4311.
36. Crimmins, F. T., "The Vapor Pressure of Pentaerythritoltetranitrate (PETN) In the Temperature Range of 50 to 98 Degrees Centigrade," Report UCRL-50704, July 11, 1969, Lawrence Radiation Laboratory, University of California, Livermore, California.
37. Edwards, G., "The Vapor Pressure of 2,4,6 - Trinitrotoluene," Transactions of the Faraday Society, Vol. 46, Part 3, March 1950, pp. 423-427.
38. Reference 20, pp. 597-601.
39. "Engineering Design Handbook, Military Pyrotechnic Series, Part 3- Properties of Materials Used In Pyrotechnic Compositions," Pamphlet AMCP 706-187, October 1963, pp. 211-213, U. S. Army Materiel Command, Wash., D. C.
40. Ibid., pp. 259-265.
41. "Handbook of Chemistry and Physics," 45th ed., The Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, pp. B-149, B-187.
42. Roberts, R. W. and Vanderslice, T. A., "Ultrahigh Vacuum and Its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1963, pp. 85-90.
43. Cox, J. M., Wright, B. A., and Wright, W. W., "Thermal Degradation of Fluorine Containing Polymers. Part I. Degradation In Vacuum," Journal of Applied Polymer Science, Vol. 8, 1964, pp. 2935-2950.

44. Cox, J. M., Wright, B. A., and Wright, W. W., "Thermal Degradation of Fluorine Containing Polymers. Part II. Degradation In Oxygen," *Journal of Applied Polymer Science*, Vol. 8, 1964, pp. 2951-2961.
45. Zapp, J. A., "Toxicity of Plastics and Resins," *Archives of Environmental Health*, Vol. 4, March 1962, pp. 342-346.
46. Deskin, R. C., "High Temperature Performance of Viton," *Viton Bulletin No. 8*, October 1961, Dupont, Inc., Elastomer Chemicals Dept., Wilmington, Del.
47. Montermoso, J. C., "Fluorine-Containing Elastomers," *Rubber Chemistry and Technology*, Vol. 34, No. 5, 1961, pp. 1521-1552.
48. Deskin, R. C. and Moran, A. L., "Engineering Properties of Viton," *Viton Bulletin No. 9A Revised*, July 1969, Dupont, Inc., Chemicals Dept., Wilmington, Del.

TABLE 1 Primary explosives surveyed.

Common Name	Acronym	Chemical Formula	Melting Point, °C	End Application or Principal Use <sup>a</sup>
Lead styphnate		$PbC_6H_3N_3O_9$	exp.	IN,S,D
Barium styphnate		$BaC_6H_3N_3O_9$		IN,S,D
Lead 4,6 dinitroresorcinol(basic)	LDNR	$Pb_2C_6H_4N_2O_8$	213	D
Lead mononitroresorcinol	LMNR	$PbC_6H_3NO_4$		IN,S,D
1,3,5 tripicrylbenzene	TPB	$C_{24}H_9N_9O_{18}$	386	D
Potassium 4,6-dinitrobenzofuroxan	KDNBF	$KC_6H_4N_4O_6$	exp. 210	S
Diazodinitrophenol	DDNP	$C_6H_2N_4O_5$	157	S
Black powder		74% $KNO_3$ 10.4% S 15.6% C		IN,S,IG
Lead azide		$Pb(N_3)_2$	exp.	IN,D
Copper azide		$Cu(N_3)_2$	exp. 202	IN,IG

<sup>a</sup> IN = Initiator  
 IG = Igniter  
 S = Squib  
 D = Detonator

TABLE 2 Secondary explosives surveyed

Common Name	Acronym	Chemical Formula	Melting Point °C	End Application or Principal Use
Azobis (2,2',4,4',6,6' hexanitrobiphenyl)		C <sub>24</sub> H <sub>6</sub> N <sub>14</sub> O <sub>24</sub>	> 485	NA
Ammonium picrate	Expl D	C <sub>6</sub> H <sub>6</sub> N <sub>4</sub> O <sub>7</sub>	d. 265	
3,3' bis (methylnitramino) -2,2',4,4',6,6' - hexanitrobiphenyl	Bitetryl	C <sub>14</sub> H <sub>8</sub> N <sub>10</sub> O <sub>16</sub>	218	
1,3 diamino -2,4,6, trinitrobenzene	DATB	C <sub>6</sub> H <sub>5</sub> N <sub>5</sub> O <sub>6</sub>	290	
3,3' diamino -2,2',4,4',6,6' hexanitro-biphenyl	DIPAM	C <sub>12</sub> H <sub>6</sub> N <sub>8</sub> O <sub>12</sub>	304	MDF
1,3 bis (2,4,6 trinitrophenylamino) -2,4,6 - trinitrobenzene	Dipicryl DATB	C <sub>18</sub> H <sub>7</sub> N <sub>11</sub> O <sub>18</sub>	335	
N,N dipicrylpyromellitimide	DIPPI	C <sub>22</sub> H <sub>6</sub> N <sub>8</sub> O <sub>16</sub>	d. 370	
Dodecanitroquaterphenyl		C <sub>24</sub> H <sub>6</sub> N <sub>12</sub> O <sub>24</sub>	> 400	NA
2,2',4,4',6,6' hexanitrodiphenylamine	Hexite	C <sub>12</sub> H <sub>5</sub> N <sub>7</sub> O <sub>12</sub>	243	
Cyclotetramethylenetetranitramine	HMX	C <sub>4</sub> H <sub>8</sub> N <sub>8</sub> O <sub>8</sub>	276	D
2,2',4,4',6,6' hexanitroazobenzene	HNAB	C <sub>12</sub> H <sub>4</sub> N <sub>8</sub> O <sub>12</sub>	221	
2,2',4,4',6,6' hexanitrobiphenyl	HNB	C <sub>12</sub> H <sub>4</sub> N <sub>6</sub> O <sub>12</sub>	241	NA
2,2',4,4',6,6' hexanitrodiphenylsulfone	HNDS	C <sub>12</sub> H <sub>4</sub> N <sub>6</sub> O <sub>14</sub> S	d. 345	
2,2',4,4',6,6' hexanitrooxanilide	HNO	C <sub>14</sub> H <sub>6</sub> N <sub>8</sub> O <sub>14</sub>	d. 302	
2,2',4,4',6,6' hexanitrostilbene	HNS	C <sub>14</sub> H <sub>6</sub> N <sub>6</sub> O <sub>12</sub>	316	MDF
Potassium hexanitrodiphenylamine		C <sub>12</sub> H <sub>5</sub> N <sub>7</sub> O <sub>12</sub> K		NA
Nitrocellulose		C <sub>6</sub> H <sub>9</sub> O <sub>4</sub> (ONO <sub>2</sub> )	d.	Propellant
Nitroglycerine		C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> O <sub>9</sub>	13.2	Propellant
Nitroguanidine	NG	CH <sub>4</sub> N <sub>4</sub> O <sub>2</sub>		
2,2',2'',4,4',4'',6,6'6'' nonanitroterphenyl		C <sub>18</sub> H <sub>5</sub> N <sub>9</sub> O <sub>18</sub>	440	
2,2',4,4',4'',6,6'6'' octanitro-m-terphenyl		C <sub>18</sub> H <sub>6</sub> N <sub>8</sub> O <sub>16</sub>	> 400	
2,2',4,4',6-pentanitrobenzophenone		C <sub>13</sub> H <sub>5</sub> N <sub>5</sub> O <sub>11</sub>	320	NA
Pentaerithrytol tetranitrate	PETN	C <sub>5</sub> H <sub>8</sub> N <sub>4</sub> O <sub>12</sub>	141	
Cyclotrimethylenetrinitramine	RDX	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	204	MDF,D
Tetranitradibenzo- 1,3a,4,6a tetraazapentalene	TACOT	C <sub>12</sub> H <sub>4</sub> N <sub>8</sub> O <sub>8</sub>	378	MDF,D
1,3,5 triamino-2,4,6 trinitrobenzene	TATB	C <sub>6</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	330	
2,4,6 trinitroaniline	TNA	C <sub>6</sub> H <sub>4</sub> N <sub>4</sub> O <sub>6</sub>	190	
Tetranitrocarbazole	TNC	C <sub>12</sub> H <sub>5</sub> N <sub>5</sub> O <sub>8</sub>	296	
1,4,5,8 tetranitronaphthalene		C <sub>12</sub> H <sub>4</sub> N <sub>4</sub> O <sub>8</sub>	> 400	
2,2',4,4' tetranitrooxanilide	TNO	C <sub>14</sub> H <sub>8</sub> N <sub>6</sub> O <sub>10</sub>	d. 313	
2,4,6 tripicryl-s-triazine		C <sub>21</sub> H <sub>6</sub> N <sub>12</sub> O <sub>18</sub>	352	NA
1,3,5-tris (methylnitramino)-2,4,6-trinitrobenzene	Tristeteryl	C <sub>9</sub> H <sub>9</sub> N <sub>9</sub> O <sub>12</sub>	exp. 205	

<sup>a</sup> MDF = Mild detonating fuse  
D = Detonator  
IG = Igniter  
NA = Not Available

TABLE 3 Vapor pressure and sublimation data at 66°C

Material	Vapor pressure, P ( torr )	Sublimation rate, G ( gm/ cm <sup>2</sup> / sec)	10 yr. weight loss, W ( gm/ cm <sup>2</sup> )
HNS	2.88 x 10 <sup>-14</sup> (33)	1.93 x 10 <sup>-15</sup>	6.09 x 10 <sup>-7</sup>
DIPAM	5.02 x 10 <sup>-14</sup> (34)	3.39 x 10 <sup>-15</sup>	1.07 x 10 <sup>-6</sup>
TATB	6.46 x 10 <sup>-12</sup> (33)	3.29 x 10 <sup>-13</sup>	1.04 x 10 <sup>-4</sup>
HMX	1.51 x 10 <sup>-11</sup> (33)	8.24 x 10 <sup>-13</sup>	2.60 x 10 <sup>-4</sup>
AP	1.05 x 10 <sup>-8</sup> (35)	3.61 x 10 <sup>-10</sup>	1.14 x 10 <sup>-1</sup>
DATB	1.78 x 10 <sup>-8</sup> (33)	8.81 x 10 <sup>-10</sup>	2.78 x 10 <sup>-1</sup>
RDX	1.32 x 10 <sup>-6</sup> (33)	6.24 x 10 <sup>-8</sup>	1.97 x 10 <sup>1</sup>
TNA	1.74 x 10 <sup>-6</sup> (33)	8.36 x 10 <sup>-8</sup>	2.64 x 10 <sup>2</sup>
PETN	5.01 x 10 <sup>-5</sup> (36)	2.82 x 10 <sup>-6</sup>	8.89 x 10 <sup>2</sup>
TNT	5.62 x 10 <sup>-3</sup> (37)	2.68 x 10 <sup>-4</sup>	8.45 x 10 <sup>4</sup>

TABLE 4 Pyrotechnic propellant ingredients surveyed.

Common Name	Chemical Formula	Melting Point °C	End Application or Principal Use <sup>a</sup>
Aluminum	Al	660	S, IG, GG
Ammonium dichromate	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	d. 170	IN, IG
Ammonium perchlorate	NH <sub>4</sub> ClO <sub>4</sub>	d. 300	IN, S, IG
Barium chromate	BaCrO <sub>4</sub>		IN, S, IG
Barium nitrate	Ba(NO <sub>3</sub> ) <sub>2</sub>	592	IN, S, IG
Barium peroxide	BaO <sub>2</sub>	450	IN, IG
Boron	B	2300	S, IG, GG
Carbon	C	3500	IN, S
Cupric oxide	CuO	1326	IN, S
Diatomaceous earth	84 to 92% SiO <sub>2</sub>	1600	S
Ferric oxide	Fe <sub>2</sub> O <sub>3</sub>	1565	IN
Lead chromate	PbCrO <sub>4</sub>	844	IG
Lead peroxide	PbO <sub>4</sub>	d. 290	IN
Lead thiocyanate	Pb(SCN) <sub>2</sub>	d. 190	S, IG
Magnesium	Mg	651	IG
Molybdenum trioxide	Mo O <sub>3</sub>	795	IG
Nickel	Ni	1455	IN, S
Potassium chlorate	KClO <sub>3</sub>	356	S, IG
Potassium perchlorate	KClO <sub>4</sub>	610	IN, S, IG, GG
Potassium nitrate	KNO <sub>3</sub>	338	S, IG, GG
Silicon dioxide	SiO <sub>2</sub>	1713	IN
Teflon	[C <sub>2</sub> F <sub>4</sub> ] <sub>n</sub>	d. 250	IG
Titanium	Ti	1725	IG
Titanium hydride	TiH <sub>2</sub>	d. 400	IN, GG
Tungsten	W	3410	IG
Viton A		d. 200	IN, IG, GG
Viton B		d. 200	IN, IG, GG
Zirconium	Zr	1857	IN, S, IG

<sup>a</sup> IN = Initiator

IG = Igniter

S = Squib

D = Detonator

GG = Gas generator

TABLE 5 Qualified candidates

Secondary Explosives	Pyrotechnic Propellant Ingredients		
	Inorganic	Metal	Organic
Diaminohexanitrobiphenyl(DIPAM)	Ammonium perchlorate	Aluminum	Teflon
Cyclotetramethylenetetranitramine(HMX)	Barium chromate	Boron	Viton A
Hexanitrostilbene(HNS)	Barium nitrate	Magnesium	Viton B
Tetranitrodibenzotetraazapentalene(TACOT)	Barium peroxide	Titanium	
Nonanitroterphenyl	Carbon	Tungsten	
Octanitroterphenyl	Cupric oxide	Zirconium	
Triaminotrinitrobenzene(TATB)	Diatomaceous earth	Zirconium/ Nickel Alloy	
Diaminotrinitrobenzene(DATB)	Ferric oxide		
	Lead chromate		
	Lead peroxide		
	Molybdenum trioxide		
	Potassium chlorate		
	Potassium perchlorate		
	Pottasium nitrate		
	Silicon dioxide		
	Titanium hydride		

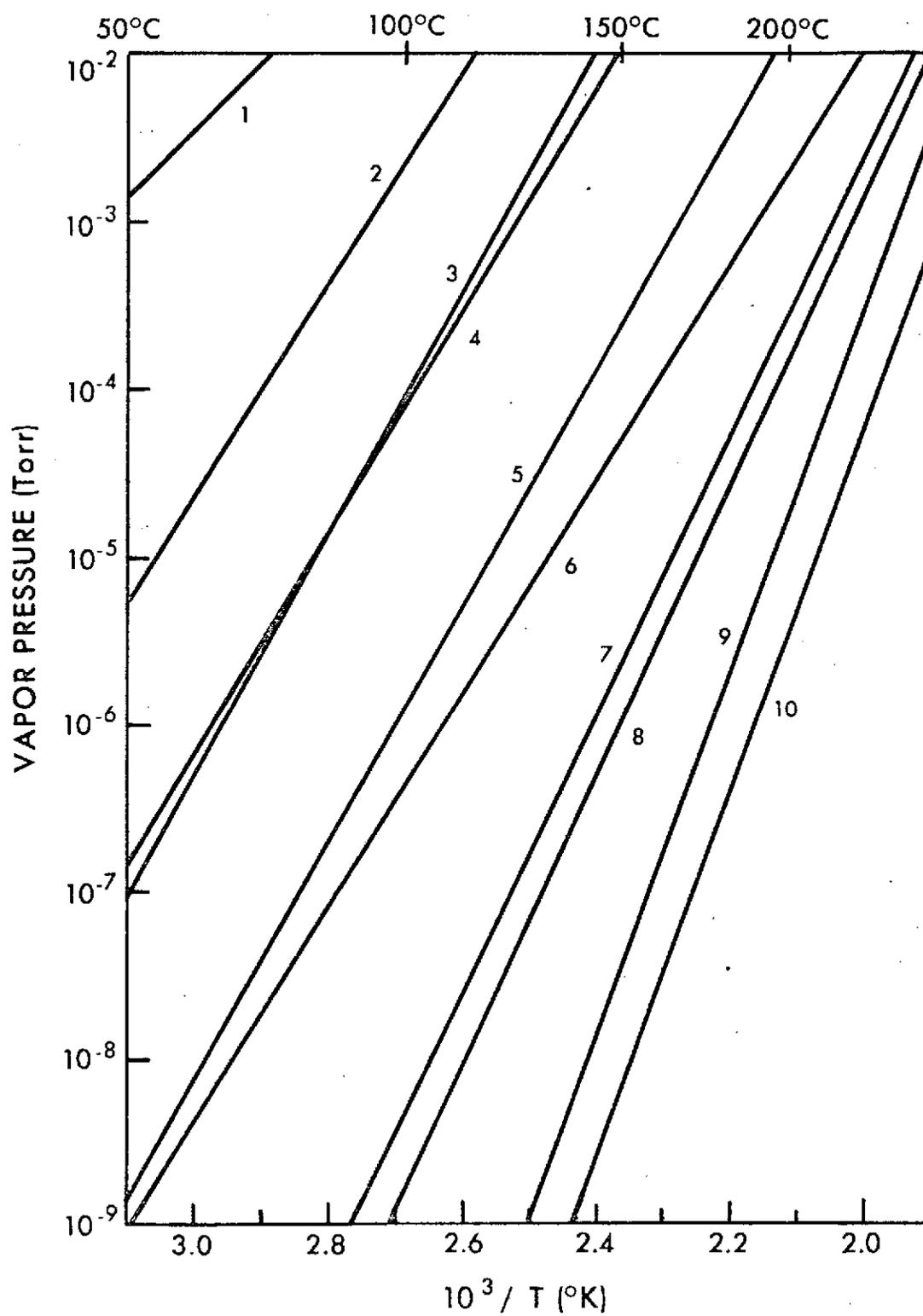
TABLE 6 Conditionally qualified candidates<sup>a</sup>

Primary Explosives	Secondary Explosives
Barium styphnate	Azobis hexanitro biphenyl
Lead dinitroresorcinol, basic (LDNR, basic)	Ammonium picrate (Explosive D)
Lead mononitroresorcinol (LMNR)	Bis(methylnitramino)hexanitro biphenyl (Bitetryl)
Lead styphnate	Bis(trinitrophenylamino)trinitrobenzene (Dipicryl DATB)
1, 3, 5 tripicrylbenzene (TPB)	
Potassium 4, 6 dinitrobenzofuroxan (KDNBF)	Dipicrylpyromellitimide (DIPPI)
	Dodecanitroquaterphenyl
	Hexanitroazabenzene (HNAB)
	Hexanitro biphenyl (HNB)
	Hexanitrodiphenylamine (Hexite)
	Hexanitrodiphenylsulfone (HNDS)
	Hexanitrooxanilide (HNO)
	Potassium hexanitrodiphenylamine
	Nitroguanidine (NG)
	Pentanitrobenzo phenone
	Tetranitronaphthalene
	Tetranitrocarbazole (TNC)
	Tetranitrooxanilide (TNO)
	Tripicryl-s-triazine
	Tris (methylnitramino) trinitrobenzene (Tristeteryl)

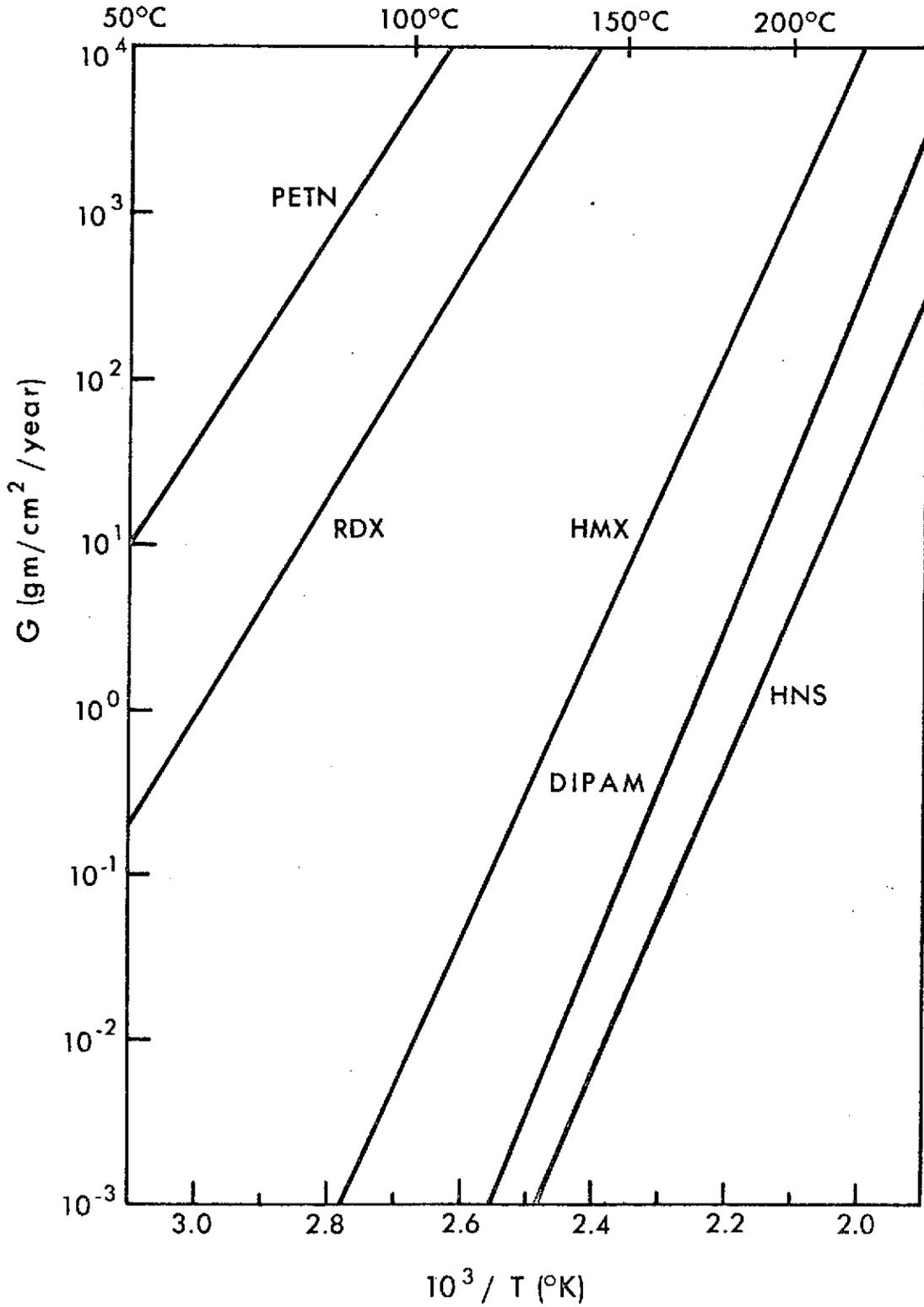
<sup>a</sup> Indeterminate without further data or testing.

## FIGURE CAPTIONS

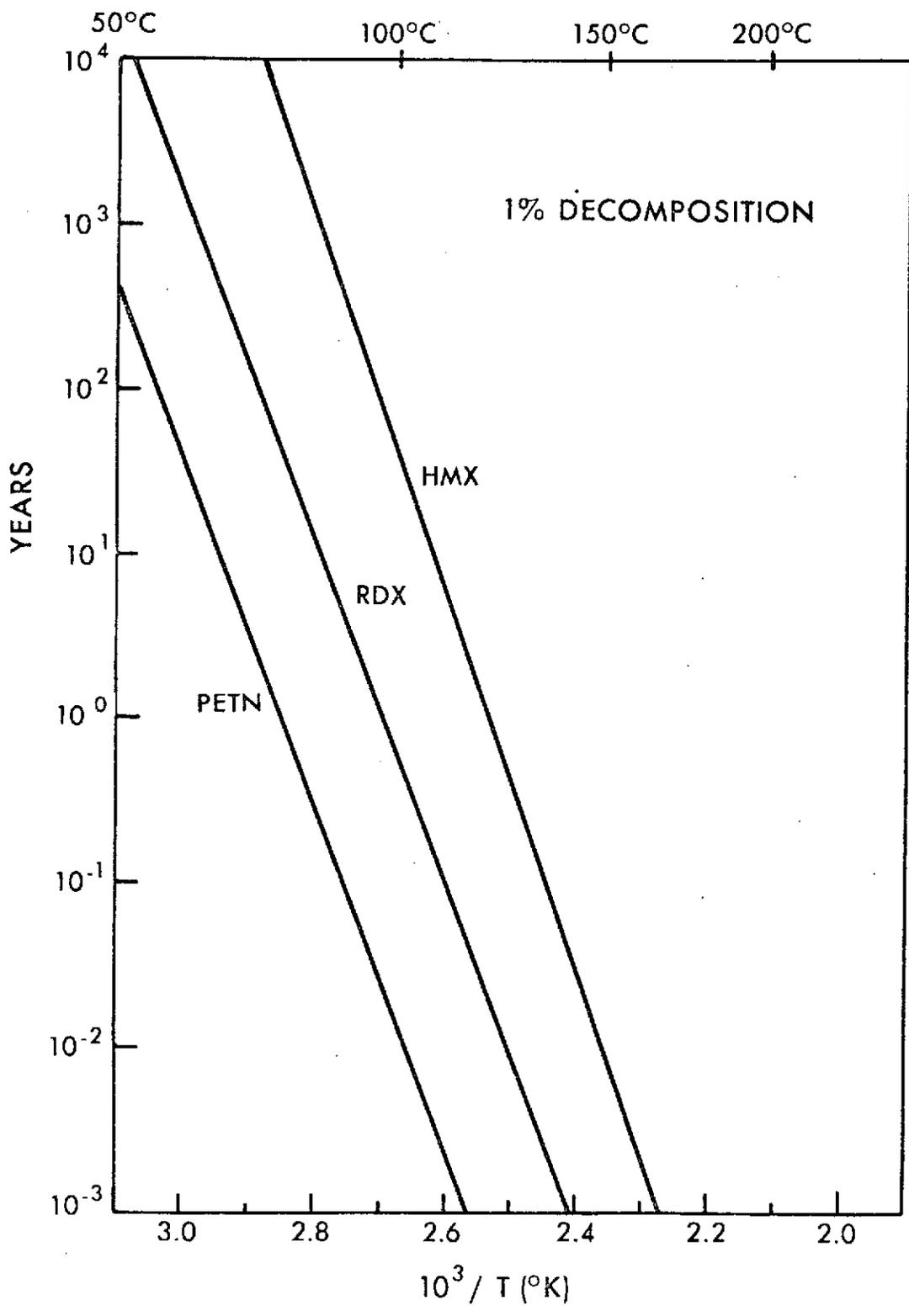
- Figure 1. Comparison of Vapor Pressures in Torr as a Function of Temperature for the Explosives (1) TNT, (2) PETN, (3) RDX, (4) TNA, (5) DATB, (6) AP, (7)  $\beta$ -HMX, (8) TATB, (9) DIPAM, and (10) HNS.
- Figure 2. Amount of Material Lost Through Sublimation, G, in  $\text{gm/cm}^2/\text{year}$ , as a Function of Temperature, for HNS, DIPAM, HMX, RDX, and PETN.
- Figure 3. Time in Years for HMX, RDX and PETN to Experience a 1% Loss Through Thermal Decomposition, as a Function of Temperature.
- Figure 4. Time in Years for HMX, RDX and PETN to Experience a 10% Loss Through Thermal Decomposition, as a Function of Temperature.



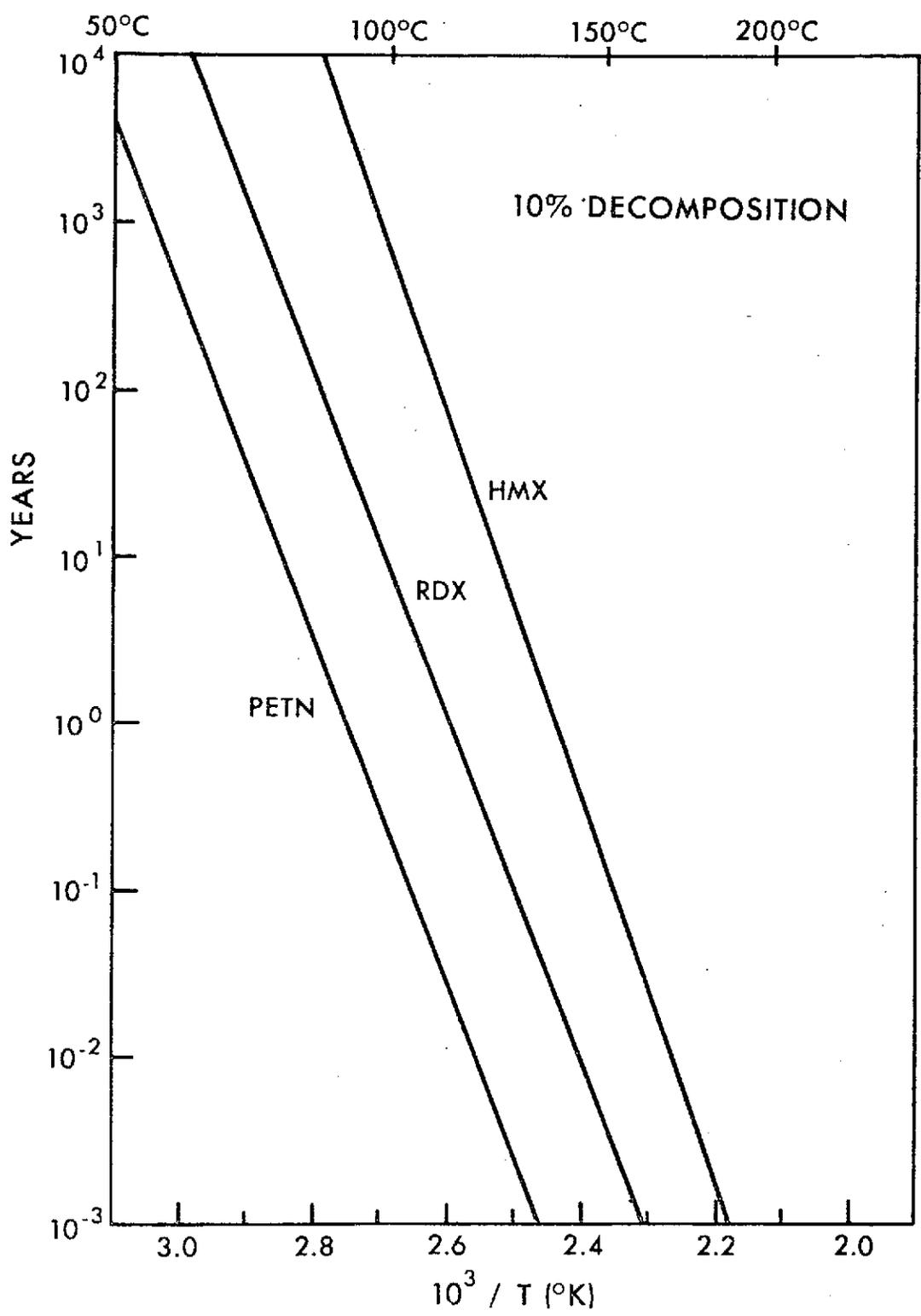
GORZYNSKI & MAYCOCK Figure 1



GORZYNSKI & MAYCOCK Figure 2



GORZYNSKI & MAYCOCK Figure 3



GORZYNSKI & MARYCOK Figure 4